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Emerging green chemical technologies for the conversion of CH_4 to value added products

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ABSTRACT

Climate change is a serious global concern in contemporary times, as the repercussions of this phenomenon occur conspicuously across the globe. Abatement of potential greenhouse gas (GHG) should be a simple and easy measure to counter the global warming. Instead, a lot of research emphasis has been put on various green technologies, through which the undesirable GHG components like methane can be converted into value added by-products. The recent promising discoveries of several methane capturing technologies at sources and of enhancing its high calorific value have surely laid a new pathway for its treatment/utilization. Here, in this review we carried out a thorough survey on many importantly emerging green technological options and their effectiveness as control measures. To this end, we explored the basic characteristics of many relevant technologies including catalytic, plasma, supercritical water, photocatalysis, membrane, solar splitting, and other relevant technologies. All of these options are surely feasible enough to process methane on one hand and to yield variety of useful chemicals as byproduct (e.g., hydrogen, methanol, formaldehyde, and aromatics) on the other hand.

Contents

1. Introduction

Over the last 50 years, more than 30% of carbon emissions and other greenhouse gases (GHG) have been released into atmosphere [1]. In fact, most of them are at all time high levels to contribute effectively to the alteration of climate conditions. It is acknowledged that climate change has already made huge negative repercussions on a agriculture, living conditions of human, and ecological systems in various modes. It is thus suspected to be too late to stop any further damage caused by climate change due to the inertia. Hence, even if GHG emissions are reduced to pre-industrial levels, average temperature is unlikely to be restored

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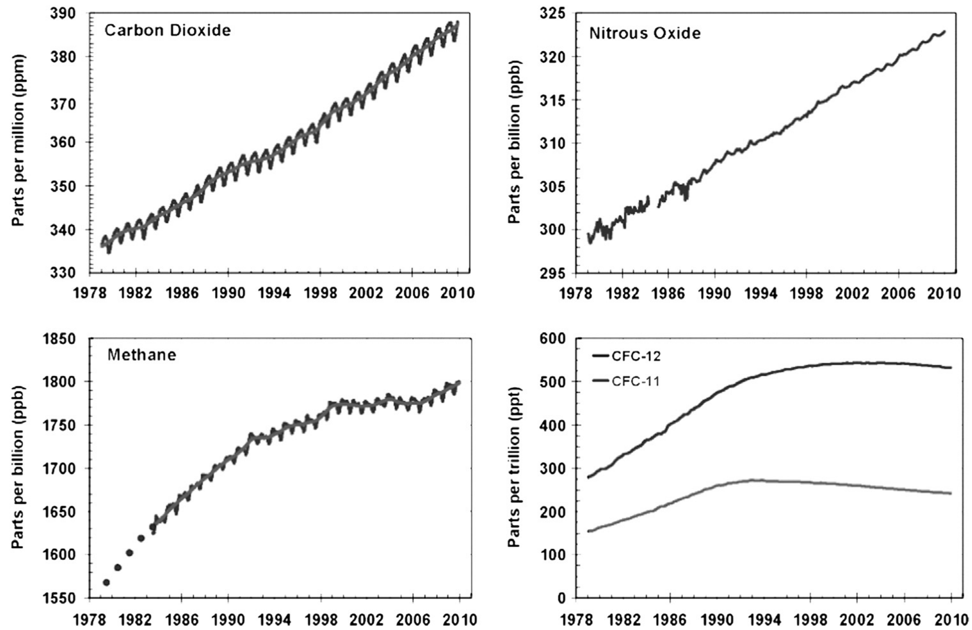


Fig. 1. Global average concentration and trend of the key GHG components [2].

any time soon. In fact, this temperature rise would impact the global population through climate-oriented disasters. According to WHO estimation, around 6–8% of global population would be severely affected by year 2030 [1]. The lifetime, global warming potential and its current levels differ for every constituent [2]. In nature, many gases can exhibit these "greenhouse" properties. Some of them occur naturally (water vapor, carbon dioxide, methane, and nitrous oxide), while others are exclusively human-made (like chlorofluorocarbons).

Among these, methane (CH_4) needs a special attention, as it is a simple hydrocarbon with high calorific value. Due to this property, its consumption as an industrial and domestic fuel source has also been greatly expanded. Its exploration as a fuel is highly desirable since it can provide alternative low carbon energy to replace coal and oil. Despite its usefulness as fuel, its presence in atmosphere as leading prominent greenhouse gas is still considered undesirable due to its involvement in climate change [3,4]. It is noted that since the arrival of the industrial era, atmospheric concentrations of methane have increased dramatically along with other major GHGs like carbon dioxide and nitrous oxide [5,6] (Fig. 1). Although the extent of methane emissions (and the associated atmospheric lifetime) is smaller than carbon dioxide, its impact on the absorption and emission of IR radiation is comparatively larger on equimolar basis. As such, the global warming potential of methane is approximately 25 times larger than carbon dioxide [7]. The global mean value of methane has reached 1800 ppb by 2010 of which value is by far greater than any other time in the past 650,000 years. Basically, the emission sources of methane share both natural and anthropogenic compartments. Natural sources include wetlands, termites, and geologic sources, whereas its anthropogenic counterparts include landfills, rice cultivation, and ruminants [8,9]. It has been proven that approximately 40% of methane emitted into the atmosphere comes from natural sources, while the remaining portion (e.g., 60%) is accounted for by anthropogenic sources (Fig. 2). This figure implies the need to cut down emissions as well as the scope to utilize them in beneficial way. On the other hand, the sinks of atmospheric methane include its destruction by moist soils or by reaction with the hydroxyl radical in the troposphere and chloride radical in the stratosphere [10–12]. As the global methane budget consists of emission from various sources, it is balanced by several sinks. Hence, a slight imbalance between the sources and sinks is likely to lead to changes in atmospheric methane levels, thus contributing to climate change processes.

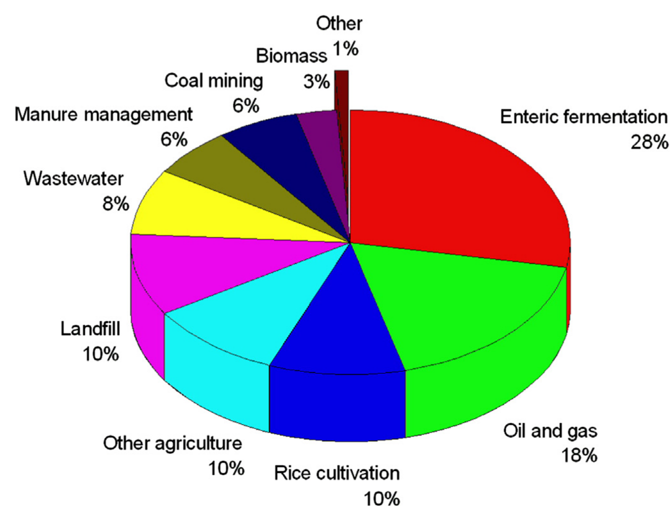


Fig. 2. Anthropogenic methane emissions from all different source sectors.

These emissions of methane into the atmosphere can be controlled by the two different mechanisms: formation control and destruction after the formation. Over the past decades, several studies surveyed major factors possibly influencing its emissions at the source [13–15]. However, methane is more unique than other GHGs in that it can also act as a source material for the synthesis of value added products. Hence, interest in its utilization methods has grown steadily with the recent discovery of its capturing technologies at various source compartments [16,17]. Thus, the efficient capture of methane from intense sources like landfills and waste water treatment plants is likely to be very realistic in the near future. However, the option of its efficient utilization still remains latent due to the complexity of methane reforming and other syngas methods and uncertainties associated

with their environmental effects. Hence, it is very essential to justify whether the technologies employed are capable of processing methane to value added chemicals or if their objectives can conform to environmental interests. The scope of this review is thus set to focus on the important characteristics of these emerging potential options for methane processing to help provide one of the practical guides for their future routes.

2. Emerging green technologies in methane processing

Green (or clean) technology is the development and application of products, equipment, and systems that can be used to conserve the natural environment and resources, while minimizing the negative impact on human activities. The most important goal of the green technology is thus to create novel methods that can promote improved productivity. In the same way, its perspective also includes innovative modifications to pre-existing practices. In the case of methane processing, extensive research has been directed to the discovery of a range of technologies that have proven feasible in terms of treatment efficiency with reduced environmental impact. Hence, in this review, we explored a number of existing and newly emerging green methane technologies that include metal and nonmetal based catalytic processes, photocatalysis, membrane technologies, plasma technologies, solar technologies, supercritical water oxidation (SCWO) technologies, etc. (Fig. 3).

As this review aims to focus on both the technical and environmental aspects of methane green technologies, in depth analyses are provided to assess the basic principles of the process, capacity, selectivity, and efficiency of diverse techniques that can be employed for the conversion of methane into value-added products. Although the practicality of those methods is yet limited, the demand for more enhanced, precise, and efficient methods expandable to large scale applications will activate the development and improvement of a cleaner methane processing. Thus, a multitude of opportunities still remain to develop greener processing technique for methane.

3. Conventional catalytic methods

In catalysis methods, a relatively small amount of foreign material called a catalyst augments the rate of a chemical reaction without being consumed in the reaction. A catalyst can make a reaction go faster and in a more selective manner. Because of its ability to facilitate reactions, a catalyst enables a chemical process to proceed more efficiently and often with less waste. Thus, in case of methane processing, catalysis based on the conventional transition metal (and other chemicals) has been recognized as a productive application through which methane can be transformed to byproducts (like methanol, hydrogen, aromatics, ethane, etc.) most of which are valuable on a commercial basis. In fact, the versatility of this technology in methane processing is increasingly well known, although not yet successful enough to be fully commercialized. The process of decomposition, oxidation, dehydrogenation, and coupling of methane by various catalysts is explained here. The major limitations of these methods are catalyst deactivation, which hampers its potential to be employed at large scale operations. Hence, the measures to improve the efficiency of these routes are currently sought actively by researchers worldwide.

3.1. Decomposition reactions to yield hydrogen and carbonaceous materials

Hydrogen is a clean energy source. The amount of energy produced during hydrogen combustion is higher than that evolved by any other fuel on a mass basis. Its heating value is estimated to be 2.4, 2.8, and 4 times higher than that of methane, gasoline, and coal, respectively [18]. It is reported that hydrogen can be produced extensively by catalytic decomposition of methane into solid carbon and hydrogen. As an endothermic process, the amount of heat needed for the activation of methane is very high, e.g., 700 °C [19]. However, the utilization of catalysts, especially the transition metals can gradually decrease the amount of heat required for activation. In the process of methane decomposition, various transition-metal based catalysts and catalyst support (such

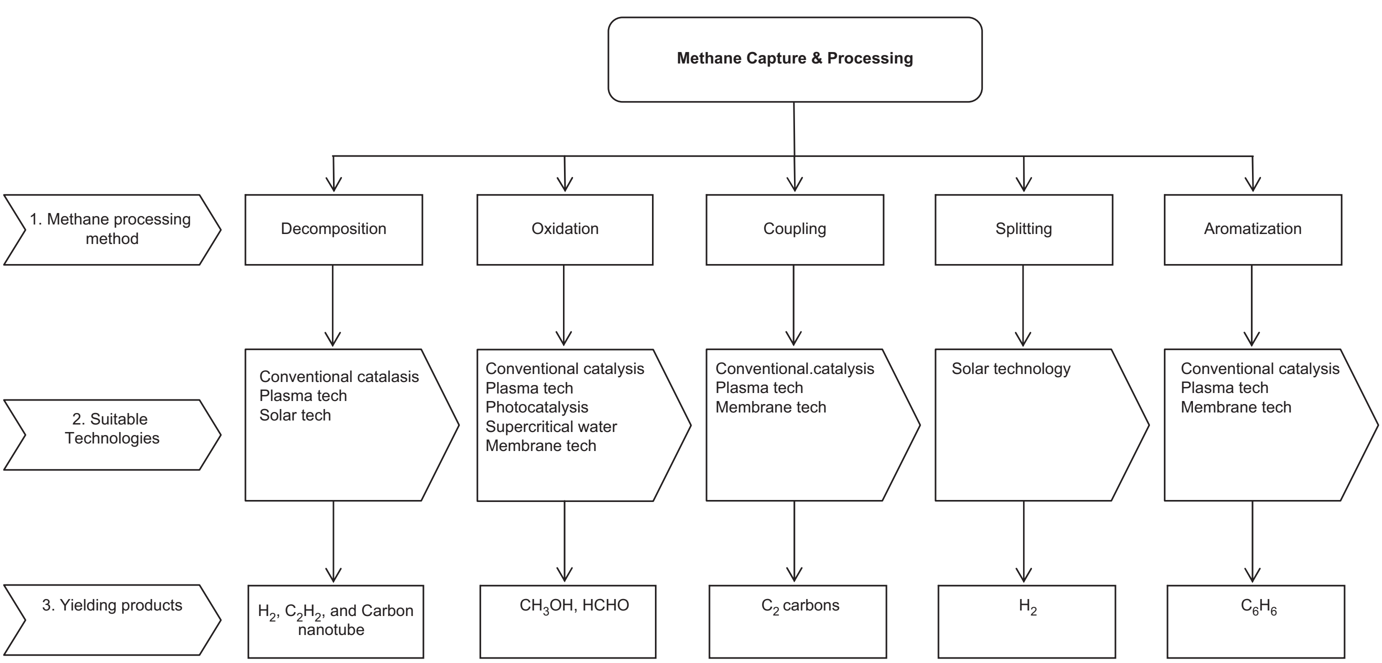


Fig. 3. Diagram of diverse conversion pathways of methane to value-added products.

as SiO_2, MgO, Al_2O_3, SiO_2–Al_2O_3, SiO_2–CeO_2, $ZnAlO_4$, and zeolites) have been used extensively. The active catalysts of this category also include the ones containing of Fe, Ni, Co, etc. Among these options, Ni-supported alumina and Ni-supported silica catalysts gained a great deal of attention. The process of methane decomposition into high purity hydrogen and carbon nanofibers was carried out over Ni/SiO_2 in a conventional gas flow reactor [20]. The initial catalytic activity and the yields of hydrogen (and carbon nanofibers) until complete deactivation of the catalysts depend strongly on the loading amount of Ni on support. The production of carbon nanofibers was reported to attain improved selectivity and yield for Ni (30 wt%)/SiO_2 [21]. Transition metal-loaded zeolites can also be used for the decomposition of methane. The Ni-loaded mesoporous Ce-MCM-41 catalyst was investigated in a micro-reactor with a fixed stainless steel bed for its catalytic performance at specified experimental conditions [22]. Its conversion level was found at 60–75% with the full (100%) selectivity of hydrogen.

In addition to chemical catalysts, some chars can also be used as a catalyst. These chars have been identified as catalysts for methane decomposition. The decomposition of methane was observed to take place in micropores of the char substance. It is reported that the lignite char is catalytically active in methane decomposition in comparison to bituminous and anthracite chars [23]. Similarly, the utilization of granular activated carbon (as a catalyst) was also proved to be feasible as a good catalyst [24].

3.2. Methanol formation by oxidation

The formation of methanol and formaldehyde from methane can be induced by its oxidation reaction [25]. The process can take place by a mechanism in which the activation of C–H bond is followed by its cleavage through electrophilic attack to yield e^+-CH_3. Then, oxidative functionalization (involving redox reactions) can yield the oxidized products of methane. It is proven that this catalytic process can take place via the highly electrophilic catalysts, which can also form a strong covalent bond with carbon. This can be achieved by a wide range of catalysts.

For instance, in the presence of a liquid catalytic system, the methane and oxidant can combine with a halogenated aqueous solvent to form methanol. Such catalytic oxidation proceeded with a conversion rate of 24.9% by binding (1) nano-particle gold (catalyst) and ionic liquids (IL) as the solvent, (2) trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAA) as the acidic reagents, and (3) $K_2S_2O_8$ as the oxidant [26]. Similarly, the process of oxidation can also be carried out heterogeneously by various transition metal catalysts. The partial oxidation of methane (to methanol and formaldehyde) by molecular oxygen has been tested in the presence of Fe-ZSM-5 molecular sieves and yielded a higher conversion rate (75%) of methane to methanol. It was also reported that increasing the temperature and contact time facilitated its conversion at the expense of the reduced selectivity to methanol. In addition, a variety of other conventional metal oxide and support based materials were also utilized as catalysts.

In recent development, the oxidation of methane to methanol was carried out with a fixed bed reactor containing V_2O_5/SiO_2 catalyst under varying experimental conditions. The results showed that the effect of pressure on methane conversion was negligible, although it influenced the selectivity of methanol. It was also proven that temperature played a vital role in its conversion into methanol. Hence, many single metal oxides, mixed metal oxides, and metal doped zeolites (like Fe, Cu-ZSM-5, and Co-ZSM-5) are all very efficient in the formation of methanol [27]. The pressure conditions and the presence of the oxidizing agents were found to have a profound influence on this process. The hurdle to the efficiency of this process lies in the activation energy of C–H bond in methane, as it requires a high endothermic energy. Another drawback of this process is that methane has a tendency to rapidly undergo deep oxidation to form carbon dioxide.

3.3. Formation of higher alkanes by coupling reactions

Conversion of CH_4 into C_2 hydrocarbons (and higher carbons) can be carried out by both oxidative and non-oxidative coupling reactions under high temperature (and ambient pressure condition). The methyl radicals formed at the surface of the catalyst undergo a gas phase coupling reaction to form ethane. Many different metal oxide catalysts, mixed oxides, and pervoskites are extensively proven to be feasible in this process. A great deal of research aiming to develop various catalysts for methane coupling started to appear in the early 1990s. Over the past three decades, various alkali-promoted oxide catalysts (oxides of Mg, Sm, Mn, and La) were tested for their oxidative coupling capacity. In the case of the alkali-promoted oxides, the selectivity for the formation of C_2 products was in the order of La < Sm < Mg < Mn [28]. Some transitional metal support catalysts were also employed to facilitate the conversion process. According to Lukyanov and Vazhnova [29], methane was converted to ethane through oxidative coupling over two platinum-supported catalysts at temperatures lower than the ones needed for conventional catalysts. Similarly a silica-based composite containing tungsten, manganese, and an alkali oxide was also used for the oxidative coupling reactions. The influence of alkali doping on the catalytic performance of the catalyst was also investigated [30]. Likewise, a series of Na–W–Mn–Zr/SiO_2 catalysts promoted by different amounts of S and/or P were prepared, and their effect on the catalytic performance was investigated for the oxidative coupling of methane. The six component Na–W–Mn–Zr–S–P/SiO_2 catalyst containing 2 wt% S and 0.4 wt% P was proven to be the optimum choice for methane coupling [31]. In another work, the effect of Na, W, Mn, Zr, S, and P on catalytic activity was also investigated. The absence of Na before the addition of Mn and Zr in the catalyst preparation depressed the formation of active species, while decreasing the activities of the catalysts [32]. In another work, $Th_{0.8}Ca_{0.2}O_{2-\delta}$ catalysts were also tested for their efficiency in oxidative methane coupling. The presence of oxide ion vacancies due to Ca ion incorporation into the ThO_2 lattice was observed; it showed high catalytic activity approaching about 24% methane conversion, which is comparable to a well-known Sr doped La_2O_3 [33]. Despite the large number of investigations reported to date, the methane coupling process is still in the development stages due to highly complicated modes of process separation. Moreover, as it needs to be operated at high temperatures, a catalyst with high thermal stability needs to be developed.

3.4. Benzene, naphthalene, and other aromatics

Methane can be converted to benzene and other aromatics. This process, while favorably occurring in the presence of oxygen, can take place by both oxidative and non-oxidative pathways. However, this is accompanied by the formation of other products (carbon dioxide, carbon monoxide, and water), when the process occurs via the oxidative pathway. The production of those products can lower the efficiency and yield rate. Hence, the processes of non-oxidative dehydroaromatization over the surface of lattice oxygen containing catalysts were also investigated. It was observed that catalytic activity decreased in the order of MO > W > Fe > W > Cr. The conversion of methane to benzene (and other aromatics) in the presence of these catalysts was observed to proceed quite actively. In addition, the dehydroaromtization of methane increased further, if combined with strong frameworks like zeolites. According to Jiang et al. [34], the

MO/HZSM-5 catalyst was found to efficiently produce aromatics from methane, while facilitating the pre-reduction of MO^{6+} to MO^{4+}. Nonetheless, it can suffer from carbon deposition on the catalyst surface [35]. The other metal-doped catalyst developed to replace MO was however less reliable in terms of stability as well as efficiency.

Bifunctional Mo/ITQ-2 catalysts have also been tested for methane dehydroaromatization [36]. The Si/Al ratio of the zeolite was known to affect the conversion of methane. The maximum activity and higher aromatics products were attained by the zeolites with a ratio of Si/Al = 15. However, if benzene is the only desired product, then Si/Al ratio = 25 was proven to be good. In a related study, two zeolites (Mo/ITQ-2 and Mo/MCM) were comparatively evaluated for their activity in methane dehydroaromatization. The results showed that the latter was more active and selective in forming aromatics, whereas the efficiency of the former was found to improve via acid treatment.

4. Plasma technologies

Plasma consists of positive, negative ions, electrons, and neutral species and is often referred to as the fourth state of matter. The majority of plasma was operated under atmospheric gas pressure. Normally, a distinction between thermal and non-thermal plasma is made at a gas temperature of 2300 K. All the chemical reactions under plasma conditions (>2300 K) are to be initiated by radicals generated by molecular dissociation due to electron impact. As such, plasma is found to have extensive applications, especially in oxidative decomposition of methane.

It has been demonstrated that plasma mediated methane decomposition occurs via the plasmalysis process using a microwave reactor under atmospheric pressure [37]. During this process, trace amounts of carbon nanopowders with very high selectivity to hydrogen were observed at the end of the reaction. The decomposition of methane in arc-jet plasma under high temperatures yielded a very large amount of carbon nanotubes [38]. Hence, it can be regarded as an efficient method to bring out large scale production of carbon nanotubes.

The oxidation of methane to yield methanol can also be carried out under plasma conditions. The conversion of methane to hydrocarbon fuels (such as methanol, formaldehyde, etc.) was achieved using pulsed discharge plasma under room temperature and atmospheric pressure [39]. In addition, acetylene was also reported to be produced from methane using non-catalytic microwave plasma technology [40]. Here microwaves of 2.45 GHz were irradiated into a cylindrical quartz reactor with the supply of methane.

Additionally, if the plasma is combined with a catalyst, it can substantially increase methane conversion efficiency. Plasma and catalyst can be modulated by using either a one-stage configuration (i.e., suspending catalyst in the plasma discharge region) or a two-stage configuration (i.e., placing catalyst in the downstream of plasma irradiation) [41]. It has been proved in innumerous studies that the application of catalytically activated plasma enhanced the efficiency and applicability of methane treatment in comparison to simple plasma application. According to Chen et al. [42], the partial oxidation of methane to methanol occurred via post-plasma catalysis using a dielectric barrier discharge under mild reaction conditions. The catalytic process involves catalytic materials such as Pt, Fe_2O_3, and CeO_2, typically impregnated on ceramic supports and air as an oxidizing agent. Among those materials, the Fe_2O_3-based catalyst showed the best catalytic activity with a methanol selectivity 36% higher than the non-catalytic system.

It was also reported that the formation of aromatics from methane can be promoted under plasma catalysis conditions. For example, a pulsed microwave plasma-assisted catalytic process converted methane to an array of aromatic hydrocarbons with benzene as a primary product at a conversion rate of 30%. The process of methane coupling, i.e., conversion to higher hydrocarbons can also be carried out. Górska et al. [43] investigated the methane coupling process in the presence of $Cu/ZnO/Al_2O_3$ bed under dielectric barrier discharge conditions, and as a result a high selectivity to ethane was observed. Similarly, other zeolites (like NaY, HY, NaX, NaA, Linde type 5A, and Na-ZSM-5) can also be used as catalysts to convert methane into higher hydrocarbons. Its products were found to include C_2 hydrocarbons like acetylene, ethane, ethylene, and carbon deposits along with other trace compounds.

5. Membrane reactor technologies

Chemical reactors made of membrane are usually referred to as a membrane reactor. This membrane reactor is a device that can simultaneously process a reaction and a membrane-based separation in the same physical device. Therefore, the membrane can play the role of both separator and reactor. There are numerous concepts to classify the membrane reactors. They are classed as extractor and distributor types based on the reactor design. In addition, the type of membranic materials (inorganic and polymeric) and the porosity of the membranes (micro, meso, macro, and dense) are also used as criteria for such classification. As low priced polymer-based membranes have low tolerance to chemicals, temperature, etc., it has relatively limited applicability. In contrast, the inorganic membrane mainly comprised with metallic or ceramic materials has greater physiochemical stability. Hence, they are more commonly used in membrane reactors.

The membrane reactor technology process was proven to be feasible for the conversion of methane to methanol, higher carbons, and aromatic compounds. However, this method has been majorly confined to methane coupling reactions for the conversion of methane to higher hydrocarbons. For instance, ionic–electronic mixed perovskite-type oxide $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ was applied as a dense membrane for oxygen supply in a reactor for methane coupling. In this work, it was reported that the conversion of methane to ethane and ethene proceeded up to 70% selectivity, but with a low rate of conversion. In another work, Wang et al. [44] used a dense membrane tube made of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) to induce the oxidative coupling of methane to C_2 compounds with a higher selectivity than conventional reactors. The impact of oxygen permeability on the methane conversion rate and hydrocarbon yield using dense $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ (BSCFO), $Ba_{0.5}Sr_{0.5}Mn_{0.8}Fe_{0.2}O_3$ (BSMFO), and $BaBi_{0.4}Fe_{0.6}O_3$ (BBFO) membrane disks with Pt/MgO catalysts was investigated. It was proven that insufficient oxygen supply can lead to poor conversions, while increasing the catalytic activity can cause a lower C_2 selectivity. Moreover, the selectivity also decreased in the BSCFO membrane reactor as the oxygen supply rate exceeded the conversion rate for the given catalyst. The oxidative coupling of methane can also be carried out on nonporous membrane film. This film consisted of PbO modified by alkaline or alkaline earth elements and porous SiO_2–Al_2O_3 tubes for PbO support. It was observed that higher hydrocarbons were successfully produced from methane with 90% selectivity. Some of the zeolite-based membranes are reported in aromatization of methane.

Enhancement of selectivity in membrane reactors depends on a variety of influencing parameters. Gozálvez-Zafrilla et al. [45] modeled the oxygen transport in a lab-scale experimental set-up for permeation testing of oxygen transport membranes using computational fluid dynamics. The conditions of such a reaction (e.g., a large gas inlet radius, short gas inlet distance, and a high

gas flow rate) were suggested to give the highest oxygen permeation flux and the lowest oxygen concentration on the membrane surface. Jăso et al. [46] demonstrated that the optimized control of oxygen feeding is a key factor for an improved C_2 yield, while a traditional fluidized bed reactor design can result in an inferior performance.

6. Photocatalysis

Photocatalysis is a photo-chemical reaction that is carried out in the presence of an external energy source (such as light). Over the last two decades, scientific interest in this area has grown rapidly, and there has been a significant technology advancement. Semiconductor photocatalysis with a primary focus on TiO_2 has been applied to a wide array of environmental applications. It has a great potential utility for reducing water and air pollution. A number of semiconductors (e.g., TiO_2, ZnO, Fe_2O_3, CdS, and ZnS) were found to act as sensitizers for the light-induced redox process due to their electronic structure, which is characterized by the filled valence band (VB) and empty conduction band (CB). When a visible or UV light source is absorbed by the surface of a semiconductor (like TiO_2), the electron present in the valence band of TiO_2 is excited to the conduction band. As a result, the electron excites from the VB to the CB band, leaving positive energy holes in the valence band. The hole formed in this process is hydroxylated by water to form the OH^* radical. Thus, the valence band hole can act as an oxidizing agent, while the conduction band acts as a reducing center. This redox capacity of the semiconductor is thus important in various environmental cleanup operations [47].

Photocatalysis has been recognized as a promising tool for methane processing. It was very efficient in the conversion of methane to methanol and C_2 compounds [48]. The hydroxyl radical on the surface of photocatalysts can be bound with methane to form a methyl radical. Then, the methyl radical reacts with additional water to produce methanol and hydrogen. The photocatalytic conversion of methane to methanol was carried out at room temperature by the utilization of WO_3 photocatalyst under visible laser light [49]. The main products of such reactions include methanol, O_2, and CO_2. In addition to visible and UV as radiation source, the utilization of a laser light has also been proven effective for photocatalytic conversion of methane. The laser-induced conversion of methane to methanol over semiconductor photocatalysts (WO_3, TiO_2, and NiO) was also studied under UV (at 355 nm). Methanol and hydrogen were the by-products formed at the end of this experimental study [50].

The performance of various photocatalysts deposited on porous surfaces (like silica and zeolites) has been actively investigated. The direct conversion of methane to higher hydrocarbons or hydrogen was examined using cerium photocatalysts [51]. Likewise, both silica- and aluminum-supported cerium catalysts were studied under xenon lamp irradiation. It was observed that hydrogen along with hydrocarbons was generated in a low dose of cerium, whereas the hydrogen production was not observed at a high dose of cerium. The process of photo-induced non-oxidative coupling of methane over H-form mordenite and ZSM-5 was found to yield ethane and hydrogen.

7. Solar technologies

Solar energy, radiant light, and heat from the sun, which can be harnessed by various methods, have been the key components in emerging green technologies. In fact, solar light plays a pivotal role in energy generation required for driving chemical processes in direct/indirect ways. Accordingly, methane processing can be carried out by utilizing solar light in numerous approaches like solar driven splitting, decomposition, thermolysis, solar chemical reactors, etc. Solar methane splitting through which methane is split into hydrogen and carbon is a highly attractive method of utilizing sunlight. Kogan and Kogan [52] performed solar thermal methane splitting in a series of tests with an unseeded low capacity reactor to produce hydrogen and carbon. In the same way, the methane decomposition reactions can also be carried out. The decomposition of methane, conducted in the absence of gaseous oxygen, mainly yielded gases like hydrogen and CO with a very small quantity of CO_2 [53]. Likewise, in the presence of solar energy, the single-step thermal decomposition of methane was studied without employing any catalyst; this process was seen to produce both hydrogen and high-grade carbon black (CB) [54]. It has been an unconventional route for hydrogen production from solar energy, as solid carbon is sequestered without emitting carbon dioxide. Solar thermolysis of methane can also be carried out to produce hydrogen by utilizing carbon particles as solar radiation absorbing agents inside the reactor [55].

The employment of solar chemical reactors is very unique and may have a crucial role to play in the future development of methane processing. The high temperature nozzle type solar chemical reactor was developed to absorb the solar radiation by a graphite nozzle and to transfer to the flow of reactant [56]. The conversion rate of methane, which can go up to 99% with a hydrogen yield of 90%, was dependent on such variables as the intensity of solar input, geometery of the graphite nozzle, gas flow rate, etc. A high-temperature solar reactor was also developed for co-producing hydrogen-rich gas and high-grade carbon black from concentrated solar energy and methane. Carbon black was recovered in the carbon trap, and the maximum chemical conversion of methane-to-hydrogen and carbon black was 95%. A high-temperature fluid-wall solar reactor was developed for the production of hydrogen from methane cracking [57]. According to this approach, the conversion of methane and yield of H_2 exceeded 97% and 90%, respectively. Such reactions depended strongly on temperature, fluid-wall heat transfer rate, and reaction surface area. The thermal decomposition of methane into C and H_2 was carried out using a 5 kW particle-flow solar chemical reactor consisting of a solar furnace in the 1300–1600 K range [54]. Although a solar-to-chemical energy conversion efficiency is expected to reach a maximum value of 31% for a pure methane flow, the actual efficiency of 16% was experimentally demonstrated. Recently, Rodat et al. [58] developed a medium-scale solar reactor (10 kW) based on the indirect heating concept, composed of a cubic cavity receiver (20 cm-side), which absorbed concentrated solar irradiation through a quartz window (a 9 cm-diameter aperture). Acetylene (C_2H_2) was the most important by-product, with a mole fraction of up to about 7%, depending on the gas residence time.

8. Supercritical methods

The supercritical method for conversion of methane is one of the promising options for methane treatment. Supercritical water is the fluid that is over the critical point of vapor–liquid coexistence state. The properties of a supercritical fluid are a mixture of both liquid and vapor phase in terms of density, viscosity, heat conductivity, and diffusion rate. Under the supercritical conditions, properties of water (such as viscosity and dielectric constant) can be readily manipulated between gas-like and liquid-like values by varying its pressure and temperature.

In case of methane processing, the feasibility of methanol production from the partial oxidation of methane in near-critical and supercritical water (at temperatures of 349 and 481 °C,

respectively) was evaluated at holding times between 1 and 9 min [59]. Under these conditions, methane and oxygen conversions proceeded up to 6% and 100%, respectively. However, very low methanol selectivity was observed, while carbon monoxide and carbon dioxide were the major products. The direct partial oxidation of methane to methanol in supercritical water (SCW) was carried out in isothermal reactor at 400–450 °C and 250 bar. Methane was then converted into CO, CO_2, methanol, and hydrogen [60]. In addition, the utilization of catalysts can enhance the efficiency of the SCWO process by increasing the methane conversion rate. The catalyzed SCWO was found to influence the conversions, selectivity, and reaction temperature of methane oxidation. Thus, selective conversion of methane to methanol has been accomplished by the catalytic partial oxidation of methane over Cr_2O_3 in SCW. In this work, several other factors were also found to influence the supercritical oxidation of methane. The presence of excess water can inhibit the methane conversion, while promoting the yield of methanol. It was also reported that increasing oxygen concentration has resulted in a reduction in methane conversion. Although the utilization of SCW in methane processing was actively carried out two decades ago, the research did not progress sufficiently over the time due to limitations in the development of this technology.

9. Other methane processing technologies

In addition to the aforementioned methods, certain electrochemical as well as biological methods have also been recommended and proven to be applicable in methane conversion. For instance, Rey and Middleton [61]carried out oxidative coupling of methane in a solid-state electrochemical reactor containing yttria-stabilized zirconia (YSZ) as an electrolyte in the presence of three different catalyst–electrode systems. These systems are based on silver and two trimetallic formulations of Mn-modified alkali (Na and K) tungstates supported on silica. It was observed that electrochemically-supplied oxygen gave higher overall C_2 selectivities than the co-fed method. The method was able to yield C_2 selectivity (86% at 4% C_2 yield) in the presence of a K-tungstate catalyst. In another work, Lee and Hibino [62] performed the direct oxidation of methane to methanol at low temperatures in a fuel cell type reactor. The trace amount of methanol production was observed at Pt/C anode at 50–250 °C, whereas among other non-platina and non-carbon catalysts, a good amount of methanol over V_2O_5/SnO_2 anode was observed after supply of methane and air. The current efficiency and selectivity of such approach toward methanol was as high as 61.4% and 88.4%, respectively.

10. Conclusion

Methane is very unique in its properties relative to other GHGs in various aspects. To date, methane has been the target of either reduction at emission source or consumption as a fuel. If its decomposition can lead to the release of carbon dioxide, the ultimate aim of greenhouse abatement technology is not completely met in such practice. Additionally, if the potential of methane is proven as precursor of value added products, there is no real reason in controlling its proliferation at some sources.

The breakthrough in capturing technologies for methane is surely an encouraging point which can eventually lead to high commercial benefits in energy, industry, and laboratory sectors with a zero capital or minimum investment. It should be noted that methane is abundant as natural byproduct of many waste products. Although research efforts directed to the conversion of methane to value added-chemicals have a relatively long history, the practicality of such applications for large scale operations surely demands a rapid progress with the aid of source capture technologies.

In this article, we discussed all the potential green technological options that have been proven to be feasible in the conversion of methane to value-added products. It is very evident that further improvement of these technologies is highly demanding; as many of such applications under the real emission conditions are in early stage of development, the scale of their operation requires expansion to acquire practicality. Advancement in these green chemical technologies would eventually help resolve issues associated with environmental destruction, while adding high commercial benefits. Hence, we conclude that this research subject will attract growing attention from researchers in environmental and energy sections worldwide in the coming years.

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